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SUPERSENSITIZED SILVER HALIDE PHOTOGRAPHIC EMULSION

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Int. Cl. G03c 1/14
U.S. Cl. 96—126 10 Claims

ABSTRACT OF THE DISCLOSURE

A spectrally sensitized silver halide photographic emulsion, having improved sensitivity in the red-sensitive region, yet no increase in fogging, comprising a combination of a pentamethinecyanine-type dye and an aromatic heterocyclic compound having a thio-keto structure is disclosed.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to a spectrally sensitized silver halide photographic emulsion and more particularly to a silver halide photographic emulsion sensitized by at least one sensitizing dye and an organic compound in a super sensitizing combination.

(2) Prior art

As a technique of making a photographic emulsion, a method of spectral sensitization has been employed comprising adding a certain sensitizing dye to a silver halide photographic emulsion to extend its sensitivity toward the longer wave length side. This spectral sensitization is markedly affected not only by the chemical structure of the sensitizing dye contained in the emulsion, the property of the silver halide micro-crystal in the emulsion, for example, the halogen composition, the crystal system, and the silver ion concentration, and the pH of the emulsion, but also by the additives such as stabilizers, antifoggants, coating agents, hardeners and color formers, present in the emulsion. Many of these added compounds generally weaken the spectral sensitivity. However, as is well known, the use of a combination of a sensitizing dye and a specific organic compound serves to strengthen spectral sensitization. This is called "super-sensitization." An organic compound imparting a super sensitizing action to a certain sensitizing dye must have a remarkably selective chemical structure. It is also necessary in selecting such an organic compound to take into consideration the influence of the properties of the emulsion. Therefore, the most important problem in spectral sensitization is to find an organic compound which will supersensitize.

It is a principal object of the invention to obtain, in spectral sensitization, a highly red-sensitive and stable silver halide emulsion of which the spectral sensitivity of the emulsion is raised without the formation of fog.

A red-sensitive silver halide photographic emulsion is required in a light-sensitive material for color photography. In particular, pentamethinecyanine dyes are used in order to obtain a silver halide photographic emulsion having no sensitivity in the green-sensitive region and a high red-sensitivity only. Generally, pentamethinecyanine dyes tend to cause fogging more readily and have a lower

spectral sensitivity than monomethinecyanine dyes and trimethinecyanine dyes. In some case, pentamethinecyanine dyes have a sensitivity in the green-sensitive region also due to the H-aggregate.

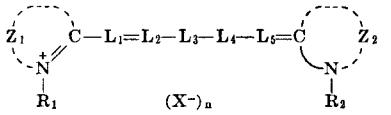
It is the further object of the invention to overcome the foregoing disadvantages of pentamethinecyanine dyes used as a sensitizing dye in silver halide photographic emulsion.

DESCRIPTION OF THE INVENTION

The above-mentioned objects of the invention can be accomplished by incorporating in combination a cyanine dye of the pentamethine type and an organic heterocyclic compound in a silver halide photographic emulsion.

The cyanine dye of the pentamethine type is represented by the following General Formula I:

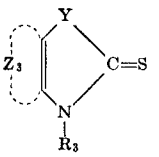
GENERAL FORMULA I



in which Z_1 and Z_2 each represents the atoms necessary to complete a heterocyclic nucleus such as a benzothiazole nucleus, a benzoselenazole nucleus, a naphthoxazole nucleus, a naphthothiazole nucleus and naphthoselenazole nucleus, and the like, L_1, L_2, L_3, L_4 and L_5 are methine groups, R_1 and R_2 are substituted or non-substituted alkyl or aryl groups, R_1 and L_1 or R_2 and L_5 may be bridged by an alkylene group, L_2 and L_4 may form a ring with carbon chain, X^- is an anion and n is 0 or 1.

The organic heterocyclic compound is represented by the following General Formula II:

GENERAL FORMULA II



in which Z_3 represents the atoms necessary to complete aromatic rings, Y is an oxygen atom, a sulfur atom, a selenium atom or

R_3 and R_4 are alkyl or aralkyl groups.

In the pentamethinecyanine dye represented by General Formula I, the heterocyclic nucleus completed by Z_1 or Z_2 can be substituted or unsubstituted. If substituted the substitution can be with an alkyl group, an aralkyl group, hydroxyl group, alkoxy group or halogen atom, R_1 or R_2 is an alkyl group such as a methyl, an ethyl, a propyl, or a butyl group, a substituted alkyl group such as a β-hydroxyethyl, a β-acetoxyethyl, an ethylsulfate, a carboxymethyl, a 2-(2-carboxyethoxy)ethyl, a β-sulfoethyl, an α-sulfopropyl, a 3-methoxy-2-(3-sulfopropoxy)propyl, a benzyl group, or an aryl group.

In the organic heterocyclic compound represented by General Formula II, the feature of the chemical structure lies in that it is an aromatic heterocyclic compound having a thio-keto structure. The aromatic nucleus completed by Z_3 is a benzene or naphthalene nucleus, e.g., the carbon

atoms in Z_3 can form a benzene or naphthalene ring. This nucleus, if substituted, can be substituted with an alkyl group, a halogen atom, a hydroxyl group, an alkoxyl group, a carboxyl group or a sulfonate group. The organic heterocyclic compound represented by General Formula II acts specifically to supersensitize the dye represented by General Formula I raising the spectral sensitivity of the dye without increasing fog formation, or fogging. On the contrary, fog formation is often reduced. Another feature is that this organic heterocyclic compound can reduce the desensitization of the sensitizing dye.

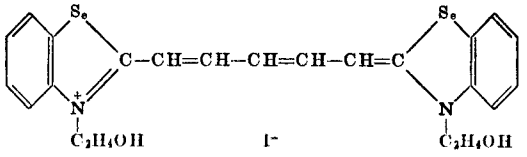
The sensitizing dye and organic heterocyclic compound used in the invention can be added to a silver halide photographic emulsion separately or together, dissolved in a water-soluble organic solvent such as methanol, ethanol or butanol. The amounts or proportions of these components can be varied depending on the properties of the other additives and the emulsion used. The added amount of the sensitizing dye represented by General Formula I to an emulsion generally ranges from 10^{-6}–10^{-3} mole per 1 mole of silver halide in the emulsion. The proportion of the sensitizing dye and organic heterocyclic compound added to an emulsion is suitably within a range of from 1:0.1 to 1:4, on a molar basis.

Typical of the silver halide photographic emulsions used in the invention are silver chloride, silver chlorobromide, silver bromide and silver iodobromide emulsions. Such emulsions can be prepared conventionally and coated onto a suitable support, such as a cellulose derivative film, a polyethylene terephthalate film, a baryta paper, other plastic films such as resin coated paper, synthetic paper or dry plate glass.

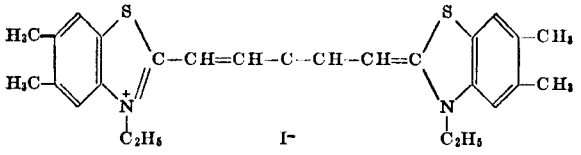
Examples of the pentamethine dye represented by General Formula I and the organic heterocyclic compound represented by General Formula II are given as follows. These examples are merely exemplary and not limiting.

GENERAL FORMULA I

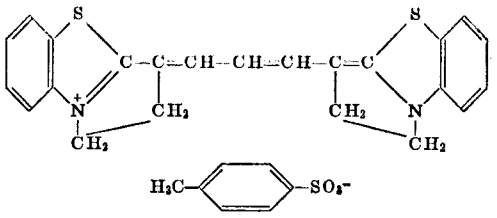
(IA)



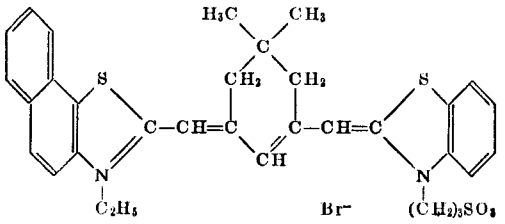
(IB)



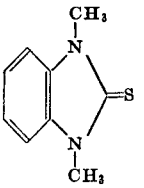
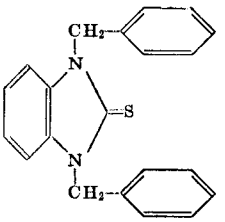
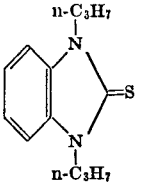
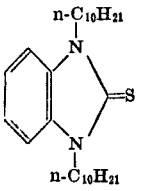
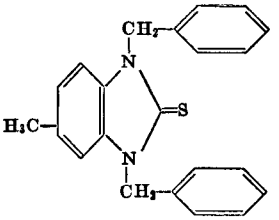
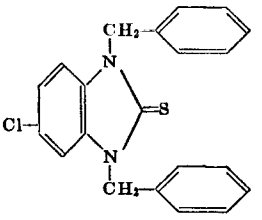
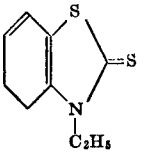
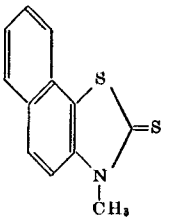
(IC)



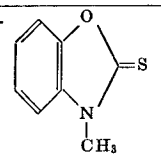
(ID)

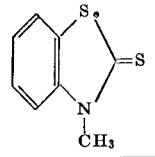


GENERAL FORMULA II

(II-A)		M.P. 151° C.
(II-B)		M.P. 191° C.
(II-C)		Liquid.
(II-D)		Do.
(II-E)		M.P. 143° C.
(II-F)		M.P. 169° C.
(II-G)		M.P. 89° C.
(II-H)		M.P. 90° C.
(II-I)		M.P. 173° C.

GENERAL FORMULA II—Continued

(II-J)  M.P. 133° C.

(II-K)  M.P. 80° C.

The pentamethine type cyanine dyes are known compounds. Methods of preparing the foregoing organic heterocyclic compounds, which can be used in the invention, are as follows.

EXAMPLE 1 (COMPOUND II-A)

Compound II-A can be obtained by a known method as disclosed in "Nippon Yakugaku Zasshi (Journal of Japan Pharmacy)," 74, 1365–1369 (1954), i.e., by reacting 2-methylthiobenzimidazole, obtained by heating under reflux 2-mercaptobenzimidazole and methyl iodide in equimolar amounts in methanol for 6 hours and then neutralizing with caustic potash, with methyl iodide in equimolar amount at 110° C. for 48 hours in a sealed tube and then heating under reflux with pyridine for 1 hour.

EXAMPLE 2 (COMPOUND II-B, E, F)

2-mercaptobenzimidazole (or a 4-substituted-2-mercaptobenzimidazole obtained by reaction of 4-substituted-1,2-diaminobenzene with carbon disulfide) and benzyl bromide in equimolar amounts are heated under reflux in methanol for 6 hours and neutralized with alkali to obtain the 2-benzylthiobenzimidazole (or the corresponding 4-substituted-2-benzylthiobenzimidazole). This material is heated under reflux with benzyl bromide in equimolar amounts in xylene for 6 hours. Then the xylene is distilled off under reduced pressure. The residue is heated under reflux in pyridine for 1 hour to give the corresponding 1,3-dibenzylbenzimidazole-2-thione (or the corresponding 4-substituted-1,3-dibenzylbenzimidazole-2-thione).

EXAMPLE 3 (COMPOUND II-C)

2-propylthiobenzimidazole obtained by heating under reflux 2-mercaptobenzimidazole and propyl iodide in equimolar amounts in ethanol for 6 hours in a manner similar to that described in Example 2 is heated and refluxed with propyl iodide in equimolar amounts in dioxane for 12 hours. After distilling off the dioxane, pyridine is added to the mixture and the mixture is heated and refluxed for 1 hour. The pyridine is distilled off under reduced pressure and the resulting yellow oily material is subjected to separation on Florisil (a synthetic resin) by column chromatography to give a colorless and transparent liquid with n-hexane used as an elutent.

Analysis of the product.—Calculated for $C_{13}H_{18}N_2S$ (percent): C, 66.64; H, 7.74; N, 11.96. Found (percent): C, 66.75; H, 7.63; N, 11.42.

EXAMPLE 4 (COMPOUND II-D)

2-mercaptobenzimidazole and decyl bromide are reacted by the method of Example 2 and the resulting yellow oily material is subjected to separation on Florisil by column chromatography to give a colorless and transparent liquid from n-hexane.

Analysis of the product.—Calculated for $C_{27}H_{46}N_2S$ (percent): C, 75.30; H, 10.77; N, 6.51. Found (percent): C, 76.19; H, 10.84; N, 6.00.

Compounds II-G, H, I are synthesized by the method disclosed in J. Chem. Soc. 1939, 473–476. Compound II-K by the method disclosed in J. Chem. Soc. 1939, 1762–1766, and Compound II-J by the method disclosed in J. Chem. Soc. 1939, 143–151.

EXAMPLE 5

100 g. of a silver chlorobromide emulsion prepared conventionally was placed in a beaker and melted, to which a given amount of a solution of one sensitizing dye represented by General Formula I in methanol was then added. The resulting emulsion was allowed to stand at 40° C. for 15 minutes with agitation and coated onto a glass support for a dry plate in a proportion of 7 ml. of the emulsion per cabinet size, followed by drying. On the other hand, as shown in Table 1, a given amount of a solution of a sensitizing dye represented by General Formula I and a given amount of a solution of one organic heterocyclic compound represented by General Formula II in methanol having a given concentration were weighed, mixed, added to 100 g. of a silver chlorobromide emulsion, allowed to stand, coated and dried in a manner similar to that described above to obtain a red-sensitive photographic material.

The resulting photographic materials were subjected to optical wedge exposure through a Fuji Filter No. 12 (manufactured by Fuji Photo Film Co., Ltd.), a yellow filter permitting the transmission of light having longer wavelengths than 500 mμ, developed at 20° C. for 10 minutes with a black-and-white developer, fixed, washed with water and dried. Then, the density was measured to determine the spectral sensitivity. The results obtained are shown in Table 1. The standard spectral sensitivity is 100 in the case in which 4 ml. of a solution of sensitizing dye I-B having a concentration of 5×10^{-4} mol./l., is added to 100 g. of the foregoing emulsion.

DEVELOPER COMPOSITION

	G.
Metol	0.3
Potassium metasulfite	1.4
Anhydrous sodium sulfite	38
Hydroquinone	6
Sodium carbonate monohydrate	22.5
Potassium bromide	0.9
Citric acid	0.7

Water to 100 ml.

TABLE 1

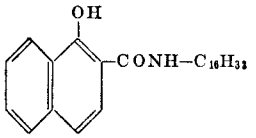
No.	Concentration (mol) and addition amount (ml.) of sensitizing dye		Concentration (mol) and addition amount (ml.) of organic heterocyclic compound		Spectral sensitivity	Fogging
1	5×10^{-4} mol/l. (I-A).	2			99	0.04
		4			85	0.05
		4	2×10^{-3} mol/l. (II-A).	1	100	0.04
		4		2	126	0.05
2	5×10^{-4} mol/l. (I-B).	2			105	0.05
		4			100	0.05
		4	2×10^{-3} mol/l. (II-B).	1	126	0.05
		4		2	156	0.05
3	5×10^{-4} mol/l. (I-C).	2			78	0.08
		4			65	0.09
		4	2×10^{-3} mol/l. (II-C).	1	82	0.09
		4		2	90	0.08
4	5×10^{-4} mol/l. (I-D).	2			105	0.04
		4			98	0.05
			2×10^{-3} mol/l. (II-E).	1	141	0.04
		4		2	118	0 04
5		4	2×10^{-3} mol/l. (II-F).	1	132	0.04
		4		2	118	0.04
6		4	2×10^{-3} mol/l. (II-H).	1	142	0.04
		4		2	159	0.04
7		4	2×10^{-3} mol/l. (II-J).	1	141	0.04
		4		2	141	0.04
		4		4	141	0.04

EXAMPLE 6

100 g. of a silver chlorobromide emulsion prepared in a conventional manner was placed in a beaker and melted, to which a mixture of a solution of one sensitizing dye represented by General Formula I in methanol and a solution of one organic heterocyclic compound represented by General Formula II in methanol were added. The mixture was allowed to stand at 40° C. for 30 minutes to stabilize the adsorption. To the mixture was added 20 g. of a coupler dispersion prepared by dissolving 5 g. of an internal type cyan coupler having the structure shown below in 10 ml. of dibutyl phthalate, and by emulsifying or dispersing in 100 g. of a 10 wt. percent gelatin solution using 2 ml. of a 10 wt. percent aqueous solution of sodium alkylbenzenesulfonate. A hardener was then added to the mixture, coated onto a film support and dried to obtain a red-sensitive photographic material for internal typecolor.

The photographic material was exposed as described in Example 1 and subjected to color forming development at 20° C. for 10 minutes, a first fixing, bleaching and second fixing to obtain a cyan negative image. Its density was measured by the use of red light to obtain the spectral sensitivity and the results are shown in Table 2.

INTERNAL TYPE COUPLER



COMPOSITION OF THE COLOR FORMING DEVELOPER

	G.
N,N-diethyl-p-aminoaniline sulfate	2.0
Sodium sulfite	2.0
Sodium carbonate monohydrate	50.0
Hydroxylamine hydrochloride	1.5
Potassoium bromide	1.0

Water to 1000 ml.
pH 10.8±0.1

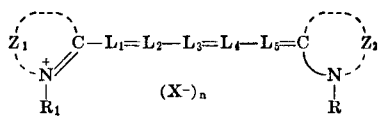
TABLE 2

No.	Concentration (mol) and addition amount (ml.) of sensitizing dye	Concentration (mol) and addition amount (ml.) of organic heterocyclic compound		Spectral sensitivity	Fogging
8	5×10^{-4} mol/l. (I-D).	2		100	0.07
		4		100	0.07
		4	2×10^{-3} mol/l. (II-B). 4	159	0.05
		4	8	142	0.04
9		4	2×10^{-3} mol/l. (II-I). 2	141	0.04
		4	4	160	0.05
		4	8	200	0.05

What is claimed is:

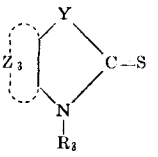
1. In a spectrally sensitized silver halide photographic emulsion, the improvement which comprises said emulsion containing a combination of:

(a) at least one pentamethine-type cyanine dye having the formula:



wherein Z_1 and Z_2 each represent the atoms necessary to complete a substituted or unsubstituted heterocyclic nucleus selected from the group consisting of a benzothiazole nucleus, a benzoselenazole nucleus, a naphthoxazole nucleus, a naphthothiazole nucleus or a naphthoselenazole nucleus, wherein said substituent is selected from the group consisting of an alkyl group, an aralkyl group, a hydroxyl group, an alkoxyl group and a halogen atom; wherein L_1, L_2, L_3, L_4 and L_5 each are methine groups; wherein R_1 and R_2 each represents a member selected from the group consisting of an alkyl group, a hydroxyalkyl group, an acetoxyalkyl group, an alkyl sulfate group, a carboxyalkyl group, a carboxyalkoxyalkyl group, a sulfoalkyl group, an alkoxysulfoalkoxyalkyl group, a benzyl group and an aryl group; wherein R_1 and L_1 and wherein R_2 and L_2 can be bridged by an alkylene group; wherein L_2 and L_4 can form a ring with a carbon chain; wherein X^- is an anion group; and wherein n is 0 or 1; and

(b) at least one organic heterocyclic compound having the formula



wherein Z_3 represents the atoms necessary to complete a substituted or unsubstituted aromatic nucleus, wherein said substituent is selected from the group consisting of an alkyl group, a halogen atom, a hydroxyl group, an alkoxyl group, a carboxyl group, and a sulfonate group; wherein Y is selected from the group consisting of an oxygen atom, a sulfur atom, a selenium atom and $>N—R_4$; and wherein R_3 and R_4 each represnts a member selected from the group consisting of an alkyl group and an aralkyl group.

2. The silver halide photographic emulsion of claim 1 wherein the aromatic nucleus completed by Z_3 is selected from the group consisting of a benzene nucleus and a naphthalene nucleus.

3. The silver halide emulsion of claim 1 wherein the cyanine dye is present at a molar ratio of from 10^{-6} to 10^{-3} to the silver halide.

4. The silver halide emulsion of claim 3 wherein the cyanine dye and the heterocyclic compound are present in a molar ratio of from 1:0.1 to 1:4.

5. The silver halide photographic emulsion in which the spectral sensitivity in red-sensitive region has been specially raised without promotion of fog formation by the presence therein of a dye and organic heterocyclic compound in combination as claimed in claim 1.

6. A photographic light-sensitive element comprising a support having thereon at least one layer of the silver halide photographic emulsion of claim 1.

7. A method of increasing the spectral sensitivity in the red-sensitive region without increasing fog formation of a photographic emulsion comprising incorporating into said emulsion the cyanine dye of claim 1 and the heterocyclic compound of claim 1.

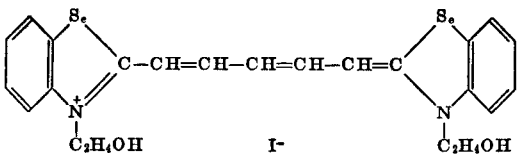
8. The silver halide photographic emulsion of claim 1 wherein R_1 and R_2 each represents a member selected from the group consisting of:

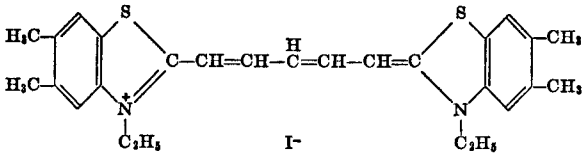
(a) an alkyl group selected from the group consisting of a methyl group, an ethyl group, a propyl group and a butyl group;

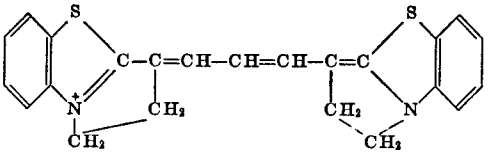
(b) a substituted alkyl group selected from the group consisting of a beta-hydroxyethyl group, a beta-acetoxyethyl group, an ethylsulfate group, a carboxymethyl, a 2-(2-carboxyethoxy)ethyl group, a beta-sulfoethyl group, an alpha-sulfopropyl group and a 3-methoxy-2-(3-sulfopropoxy)propyl group; and

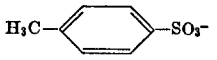
(c) a benzyl group.

9. The silver halide photographic emulsion of claim 1 wherein said pentamethine-type cyanine dye is selected from the group consisting of

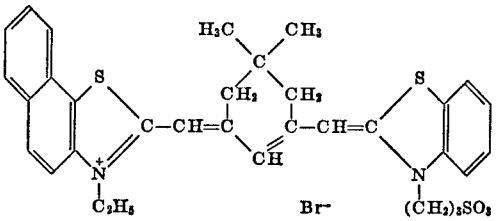




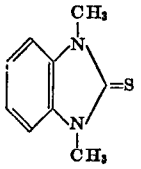


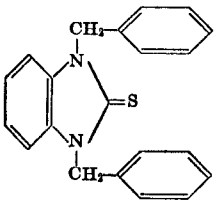


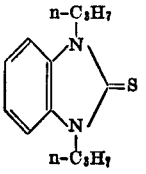
and

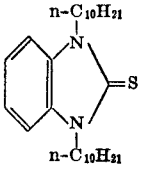


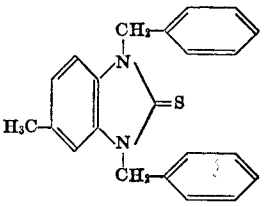
10. The silver halide photographic emulsion of claim 1 wherein said organic heterocyclic compound is selected from the group consisting of

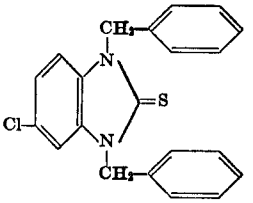


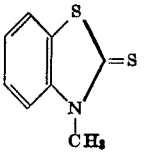


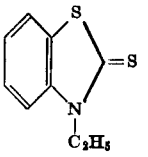


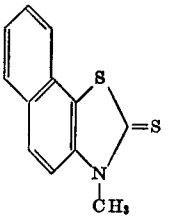


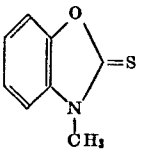












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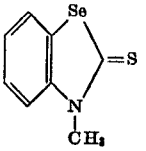

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U.S. Cl. X.R.

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